TRANSPORT PROPERTIES OF SEVERAL AMORPHOUS SEMICONDUCTORS

Virgil Glenn Cox

TRANSPORT PROPERTIES OF SEVERAL AMORPHOUS SEMICONDUCTORS

by

Virgil Glenn Cox

S.B., Massachusetts Institute of Technology
(1962)

SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
[E.E.]
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1972

TRANSPORT PROPERTIES OF SEVERAL AMORPHOUS SEMICONDUCTORS

by

Virgil G. Cox

Submitted to the Department of Electrical Engineering on May 12, 1972 in partial fulfillment of the requirements for the degree of Master of Science.

- -

ABSTRACT

Electrical resistivity and thermoelectric power were measured for the $(1-x)As_2Se_3{:}x\ Sb_2Se_3$ system for $x = 0.0$, 0.2 and 0.4 over the temperature range 25°C to about 190°C. The resistivity activation energy and thermoelectric power activation energy were shown to be equal to within experimental accuracy for $x = 0.0$ and 0.2. For $x=0.4$ it is tentatively concluded that the activation energies are also the same for both processes, although the possibility of partial devitrification of the sample during the experiment precludes a more definitive statement at this time.

Samples of $(1-x)As_2Se_3{:}x\ Sb_2Se_3$ were cut from hollow cylindrical ingots. These ingots were prepared by air quenching rotating evacuated Vycor cylindrical ampoules which contained appropriate mixtures of As, Sb and Se. The samples were placed in a sample holder in an evacuated tube in a furnace. A temperature gradient could be established by heating one end of the sample holder. Resistivities were calculated using the value of the current measured by an electrometer in series with a battery and the sample. Thermoelectric power data were obtained by using the standard differential technique using an electrometer to measure the sample emf and thermocouples to measure the temperature gradient.

Resistivity activation energies were established to be 0.94±0.03eV for x = 0.0, 0.84±0.03eV for x = 0.2 and 0.76±.06eV for x = 0.4. The resistivity was found to be 1.8x10^{12} Ω cm for x = 0.0, 1.7x10^{11} Ω cm for x = 0.2 and 3.7x10^{9} Ω cm for x = 0.4 at 298°K. The thermoelectric power was determined to be positive for all samples and have a magnitude of 1.43±.05mV/°K for x = 0.0, 1.94±.05mV/°K for x = 0.2 and 1.38±.05mV/°K for x = 0.4 at 333°K. The thermoelectric activation energies were found to be 1.03±.08eV for x = 0.0, .78±.12eV for x = 0.2 and .49±.10eV for x = 0.4.

Samples were found to exhibit polarization effects when subjected to fields of about 100 volts per centimeter, but this phenomenon was not investigated in detail.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to, Professor D. J. Sellmyer for his encouragement and concern through out this investigation.

Special thanks are due Professor D. Adler for guidance and suggestions which helped to keep the thesis work managable.

To my wife, Patricia, I wish to express my deep appreciation for her help, support and tolerance, for without her aid this thesis would not have been completed.

I would also like to thank the Advanced Research Projects Agency for funding this work.

TABLE OF CONTENTS

LIST OF SYMBOLS

Symbol	Name
A	Area
C	Coefficient of conductivity
e	Charge on an electron
E_c	Energy of the edge of the conduction band
E_F	Fermi Energy
E_s	Thermoelectric activation energy
E_V	Energy of the edge of the valance band
E_ρ	Resistivity activation energy
I	Current
k	Boltzman constant
l	Active length of sample
R	Resistance
S	Thermoelectric power, Seebeck voltage
T	Temperature
V	Voltage
α	Optical temperature coefficient
κ	Thermal conductivity
Ω	Ohms
ρ	Resistivity

γ	Thermoelectric power temperature coefficient
σ	Conductivity

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

Amorphous materials, to distinguish them from other classifications, are simply those materials which display only short range atomic order. The word amorphous is normally, but not always, associated with solids, vice gels, liquids or vapors. The amorphous state is a metastable state and may be created by many techniques, including vapor deposition, desicating gels, radiating, shearing or reacting solids or quenching melts. The last technique, quenching, is most commonly associated with glasses. The amorphous glass is also said to be in the vitreous state. Nomenclature in this field is still a problem. In fact, researchers in the field have not fully agreed as yet on a method of classification of non-crystalline solids.(1)

Many amorphous materials have been well studied and their properties are quite accurately determined. As_2Se_3 is one example of a very heavily studied material with a vitreous semiconducting phase as well as a crystalline phase. However, the fact that considerable knowledge has been amassed concerning the properties of this material does not imply that all questions have been answered. To some extent

this results from experimental measurements which are insufficiently accurate to test the various theoretical models. Additionally, however, it appears that an amorphous material made by differing methods and sometimes even by the same method, (2) have different properties and this adds additional confusion.

Though some aspects of the understanding of these materials are quite well founded on both theory and experiment, there is no definitive theory yet in existence for dealing with disordered systems such as amorphous semiconductors (3). The lack of long range order apparently causes the very concept of lattice waves, which was effective in analyzing crystalline structures, to break down and no satisfactory treatment has been found for dealing with the electronic structure and transport properties of these materials.

Solid amorphous materials are of more than just academic interest since some of them have properties which may be economically exploited. Of special interest in this respect, is the "memory" capability of some of semiconductors; this comes in two variations, the memory switch and the threshold switch (2). Each variation has its own realm of special application. Threshold switches hold promise in the field of electroluminescent displays and in control and logic circuitry. Memory switches hold equal promise for use in memory devices and laser activated switching (4).

Though considerable amounts of data have been gathered concerning some properties of amorphous materials, other areas of interest are relatively unexplored. One such area concerns the effect of doping on electrical properties. For example, the addition of 1% silver is known to cause an increase in the conductivity of arsenic selenide by four orders of magnitude (5).

Bismuth selenide, Sb_2Se_3, can also be used as a dopant in As_2Se_3 and the combination of these two materials form an amorphous system over a wide range of concentration. A method for forming $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$ samples recently has been perfected (6). Since little information has been published concerning the properties of the system, excepting for $x = 0$ or 1, it seemed a proper selection for the purpose of providing additional knowledge concerning the effects of doping on the electrical properties of amorphous materials.

The objectives of the thesis work, therefore, were:

(1) To design an apparatus that would be able to be used to measure the resistivity, the thermoelectric power and the thermal conductivity between 296°K and the devitrification temperature of the samples.

(2) To make several samples of the $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$ system and to measure their resistivity, thermoelectric power and thermal conductivity.

(3) To evaluate the results in light of present knowledge and theory.

Chapter II is to provide the reader with more detailed knowledge of the existing experimental and theoretical understanding of the (1-x) $As_2Se_3 \cdot x\ Sb_2Se_3$ system. Chapter III gives the detailed experimental and analytical procedures which were used to produce the results which are presented in Chapter IV. The summary and conclusions are contained in Chapter V, and Chapter VI suggests where further work in this area might be profitable.

Chapter II

PREVIOUS WORK

A. General

1. Electrical Resistivity:

Considerable theoretical and experimental effort has been expended in the study of this property in amorphous materials. The amorphous state of a material generally has higher resistivity than the crystalline state and in the case of semiconductors the increase can be as large as several orders of magnitude. This fact, coupled with knowledge about the phase diagram, is sufficient to explain the basic mechanism behind memory switching in amorphous materials (2). The primary cause of the other switching device presently being studied, ie, the threshold switch, however, is a subject of much controversy. Even though more is known about the electrical resistivity of amorphous materials than about, e.g., the thermal conductivity, there are many unanswered questions. For example, why are the values of electrical resistivity extropolated to infinite temperature the same for corresponding crystalline and amorphous semiconductors, despite the much smaller value of the amorphous material at room temperature; why do some amorphous semiconductors

exhibit n-type Hall effects but p-type thermoelectric powers?

Bulk chalcogenide glasses which have been measured show an exponential dependence of resistivity on temperature similar to crystalline materials (over the range of temperatures covered in this experiment). However, the slope of the logrithm of ρ vs $\frac{1}{T}$ shows different "activation" energy than for the crystalline form of the same material. No unambiguous universal theoretical explanation has yet been found for this phenomenon$^{(7)}$.

Doping of amorphous materials also presents many riddles. Iodine when added to $As_{30}Se_{18}Ge_{21}Te_{31}$ to produce $As_{30}Se_{18}Ge_{21}Te_{30}I$, has no measurable affect on the resistivity, yet 1% addition of Ag to As_2Se_3 changes the resistivity by about four orders of magnitude. Arguments which explain the lack of response of the quaternary chalcogenide above fail when applied to the binary chalcogenide.

Some comments on resistivity, such as those delineated below, seem to be well documented.

i) If atoms in some chalcogenide glass are replaced by heavier isoelectronic atoms the resistivity will decrease $^{(6)}$.

ii) The resistivity of a binary chalcogenide is greater than that

of a pseudobinary (6).

iii) Electrical conductivity is electronic and not ionic and can have a contribution from a hopping mechanism via localized states as the normal bandlike type of conductivity (7).

iv) The resistivity changes in accordance with an exponential function of $(T)^{-1}$ or $(T)^{-\frac{1}{4}}$ (8).

2. Thermoelectric Power

The Seebeck coefficient or thermoelectric power has its most historical significance in temperature measurement since the voltage created by a bimetalic junction (thermocouple) in a temperature gradient is a Seebeck voltage. In metals this voltage is quite small, i.e., on the order of microvolts per degree, but in semiconductors it can be as high as several millivolts per degree. This large effect can be produced in a semiconductor because the charge carriers cannot shift as easily in a semiconductor as the free electron gas in a metal can, therefore, larger internal fields can be tolerated by the semiconductor. In intrinsic semiconductors in which the mobilities of the holes and electrons are about equal the thermoelectric power can be small. It is in materials that have

one carrier relatively immobile or suppressed by doping that a large thermoelectric power will be found.

For crystalline materials the theory of thermoelectric power is usually derived from the Boltzman transport equation. Experimental and theoretical work on thermoelectric power in crystalline materials has shown that the value is a slowly varying function of temperature (over the temperature covered by this thesis). Gubanov (9) has derived an expression for the thermoelectric power for amorphous materials. His results indicate that the thermoelectric power will have the same slow dependence on temperature as the crystalline materials had but is expected to be different because of the carrier scattering due to the lack of long-range order. Some experimental work has shown that thermoelectric power may increase as short-range order (compositional and positional) decreases. It should be pointed out that in light of what is known today, Gubanov overlooked some very important aspects of the amorphous semiconductor phenomena and his transport equations cannot be used explicity.

Thermoelectric power has been found experimentally to have some rather abrupt changes, generally in the form of a local maximum(10,11).

It has been suggested that these might be explained by either changes in the scattering terms or in the temperature dependent changes in the mobility. One thing is abundantly clear and that is that the theory does not yet provide unambiguous results or possess any ability to predict values in new materials.

B. $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$

Mixtures of As_2Se_3 and Sb_2Se_3 were amoung the first glasses to be known. Until recently however, the system did not receive very much attention except to establish glass forming regions, densities and a few isolated values for resistivity. The resistivity, ρ ,and thermoelectric power, S, were determined to be approximately $10^{12}\Omega$ cm and 1.1mV/°K in 1957 (12). At that time the activation energy for As_2Se_3 was determined from the temperature dependence of conductivity to be 1.0eV. The measurements put the resistivity of the crystalline higher than the vitreous state, a condition which is now known to be incorrect as a result to the work of Uphoff and Healy (13).

Platakis recently has done a detailed study of several of the properties of the $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$ system. His values for the resistivity and the activation energy have confirmed that the

vitreous state is more resistive than the crystalline and not less. He also measured the following values based on using $\rho = \rho_o \exp[E_\rho/kT]$ to analyze his data.

Sample	Activation Energy, E_ρ [eV]	$\log \rho_o$
As_2Se_3	0.975	-3.6
$0.8As_2Se_3 \cdot 0.2Sb_2Se_3$	0.86	-3.4
$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$	0.75	-2.9

These activation energies were within a few hundredths of an electronvolt of being one half the energy gap he measured by optical means, which indicates that the Fermi energy may be very near the center of the gap.

Callaerts, Nagel and Denayer (14) measured an E_ρ of 0.96eV and a $\log \rho_o$ of -3.8 for As_2Se_3. They also measured the thermoelectric power over the range of 293°K to 473°K. By fitting their data to an expression of the form

$$S = \frac{k}{e}\left(\frac{E_s}{kT} + B\right),$$

where

E_s = thermoelectric activation energy

B = a constant,

they found $E_s = 1.01 \pm .05\text{eV}$ and $B = -7.08$.

Between the composition $0.5As_2Se_3 \cdot 0.5\ Sb_2Se_3$ and pure Sb_2Se_3 there have been very few published results. This most likely results from the difficulty in producing a vitreous form except in thin films like those produced by Johnson and Girdart (15) in 1958. They found a resistivity of 10^4 Ω cm in the crystalline state and 10^7 Ω cm in the vitreous state, but no other studies were accomplished at that time on the amorphous state. Previous work by Braithwaite (16) on crystalline Sb_2Se_3 had established an optical energy gap of 0.95eV which is reasonably consistent with the results published by Black (17) in 1957. Black found a conductivity activation energy of 0.7eV and a resistance of $6X10^4$ Ω cm at 283°K. He also measured the thermoelectric power from 373°K to 523°K and found that it decreased linearly in 1/T from 0.9mV/°K to 0.4mV/°K as the temperature increased over that range. Chizhikov and Shchastlivyi (18) quote a value for the resistivity activation energy of crystalline Sb_2Se_3 of 1.2eV, but that value seems to be inconsistent with the other information presented above.

Chapter III

EXPERIMENTAL PROCEDURE

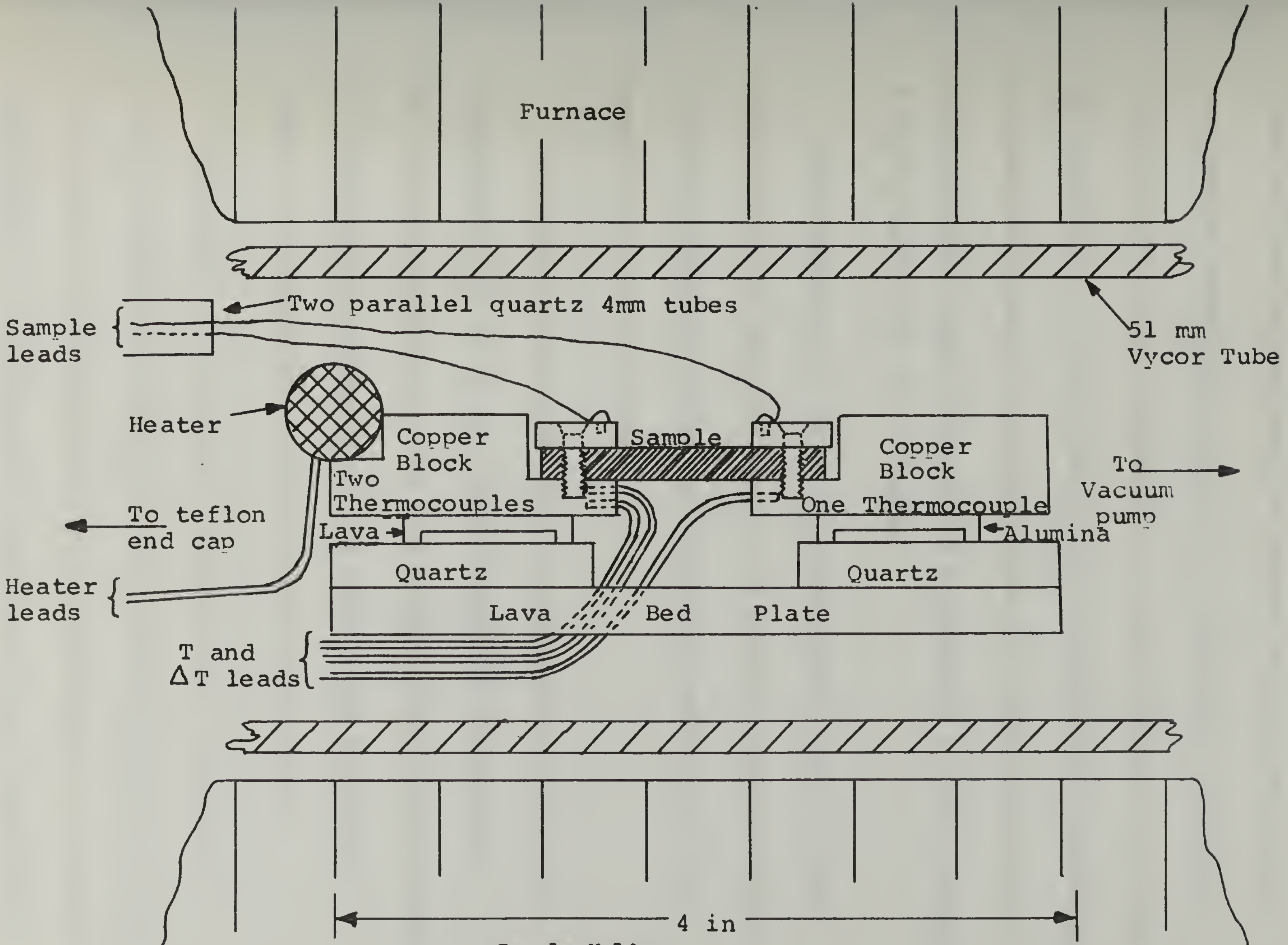
A. <u>General</u>

The original motivating force determining the geometry and physical lay out of the apparatus was a desire to measure ρ, κ and S for solid bulk materials over the temperature range of 296°K to 773°K using one sample holder and its associated leads, bed plate, etc. It was anticipated that the resistivity at 296°K would be on the order of 10^{14} ohm-cm; the thermal conductivity about 2-5 mw $(\text{deg cm})^{-1}$. It was determined by experiment that the thermal conductivity measurements could not be made without modification of the apparatus from the configuration used for ρ and S measurements. Figure 1 shows a profile of the apparatus, exclusive of the modifications needed for thermal conductivity measurements. These modifications were:

(1) Removal of the leads to the copper blocks.

(2) Installation of high emissivity insulating seperately heated blocks on either side of the bed plate.

(3) Installation of a temperature control system to keep the heated blocks at the same temperature as the furnace walls.



<u>Sample Holder</u>

Figure <u>1</u>

These modifications were required because radiative heat losses were causing unacceptable errors in the temperature distribution and in the heat input measurements. It was determined that though the geometry of the sample holder and the furnace were satisfactory for measuring ρ and S it was not optimum for thermal conductivity and, therefore, thermal conductivity measurements of the $(1-x)As_2Se_3 \cdot x\,Sb_2Se_3$ samples were not attempted.

The temperature of one of the copper blocks could be raised above that of the other by passing a DC electric current through a 10 watt 20Ω resistor, called the differential heater, which was mounted on one of the blocks.

Temperature was measured using a Keithley model 147 or 148 nanovoltmeter and one of the copper-constantan thermocouples. The two remaining thermocouples (one on each block) were connected in a differential connection so that their output was proportional to the temperature difference between the blocks.

Tests were run to determine the temperature difference between the thermocouples imbedded in the copper blocks and the end of the sample. This was accomplished by connecting two additional thermocouples in a differential connection and then clamping them

in the jaws of the copper blocks in place of a sample. The test was to let the system come to thermal equilibrium, then use the differential heater to raise the temperature of one block. Since the temperature of the other block initially did not change because of the low thermal conductivity the difference between the differential temperatures measured by the two pairs of thermocouples was the difference between the ends of the sample and the thermocouple imbedded in the block. The temperature difference as measured by the sample thermocouples was equal to that measured by the imbedded thermocouples to within ± 1.0μV. This was the case even when the system was going through a thermal transient.

The resistance and the Seebeck voltage without any sample were measured as the results were to be used to correct the measurements taken with samples when applicable. As it turned out the resistance was 2.5 orders of magnitude higher than that of the most resistive sample and the Seebeck voltage was lower than 0.01 mV/^{o}K over the temperature range used for sample measurement.

The furnace was allowed to come to thermal equilibrium using a DC power source at constant current. The temperature was not controlled during the Seebeck voltage measurements so that the

electronic transients could be avoided, however, the average temperature of the samples did not change by more than 5°K over any measurement period.

To ensure positive contact between the sample and the copper blocks, the jaws of the block which were to contact the sample were silvered with liquid silver which when dry was 0.01mm thick and served as a crushable surface for the very hard glass to imbed itself and thereby produced excellent electrical and thermal contact.

All of the external electric leads were shielded and grounded but the system still suffered from the effects of changing electrostatic fields being created near it.

A Princeton Applied Research Model 136 battery operated electro--meter was used for all the sample voltage and current measurements. The input impedance was variable from 10^2 to $10^{14}\Omega$ and the meter was calibrated using reference resistors which were accurate to within $\pm.1\%$. The meter was accurate to $\pm$ 2%. The meter was generally used in a feedback mode of operation which provided a driven guard circuit to reduce the effects of external capacitance. Another electrometer, Keithley 610C, was tested on the system but was not

successful in measuring the Seebeck voltages.

A dual channel and a six point recorder were available and were used for monitoring all the signals to ensure that thermal equilibrium had been reached and all voltages had stabalized before data was recorded.

B. Sample Preparation

Platakis(6) perfected a method for making samples of the $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$ system. The idea was that since during air quenching the ampoule cooled from the outside in, if it was rotating it would deposite the molten material in layers and thus create a hollow cylindrical shaped solid body with high homogeneity.

The materials, As, Sb, and Se were of high purity. (See Appendix A.) Two compounds, As_2Se_3 and Sb_2Se_3, were made separately by weighing the appropriate amounts to an accuracy of $\pm 10^{-5}$g and then placing the materials in cleaned Vycor ampoules. Each ampoule was evacuated to 10^{-6} torr, sealed and then heated to 1023°K for three to six hours. Then they were rotated for an additional four hours to insure mixing before they were air quenched as described above.

To make the samples for measurement (with the exception of

As_2Se_3) the above process was repeated using As_2Se_3 and Sb_2Se_3 as the constituents. Samples were made as follows:

As_2Se_3

$0.8As_2Se_3 \cdot 0.2Sb_2Se_3$

$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$

The ampoules were cut open using a diamond saw and samples were then cut from the cylinder using a string saw, thus creating samples which were segments of an annulus with parallel sides. Typical dimensions were thicknesses of 0.15 cm, lengths of 3 cm and widths of 0.3 cm. The measurements could be made to within ± 0.005 cm and, therefore, introduce an error of ± 4%.

C. Electrical Resistivity

The resistance of the sample was measured by using the electrometer in the current measuring mode. Figure 2 shows the circuit.

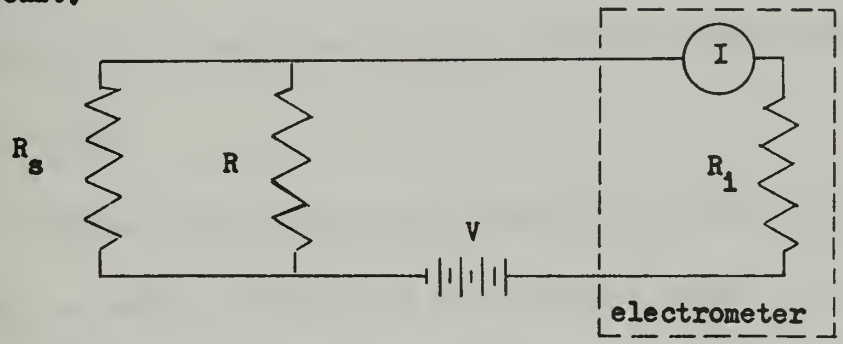


Figure 2 Resistance measurement circuit

$$R_s = \frac{R\left(\frac{V}{I} - R_1\right)}{R - \frac{V}{I} + R_1}$$

Where: $R_s = \rho A/l$

A = cross-sectional area of the sample

l = active length of the sample

R_s = sample resistance

R = resistance of parallel paths

R_1 = internal resistance of the electrometer

The theoretical magnitude of the geometric correction for fringing of the electric field was below the experimental accuracy

of the equipment and tests conducted with samples of known resistivity proved that the fringing could be neglected.

The capacitance of the circuit exclusive of the electrometer was measured at 1000 Hz and 388°K and found to be 132 pf. This resulted in a circuit time constant which was always faster than 1/10 second.

Surface contact resistance between the copper blocks and the sample material was tested by using various samples with various amounts of contact area. Under the conditions of this experiment no effect was found and it was, therefore, neglected.

As noted before, the resistance of the sample holder was 2.5 or more orders of magnitude larger than the sample resistance and the internal resistance of the electrometer could be kept to three orders of magnitude below the resistance of the sample so that the final equation becomes, therefore,

$$\rho = \frac{VA}{Il} ,$$

with an expected accuracy of ± 6%.

The distance between copper blocks was generally 1.5 cm or larger. Therefore, since the battery was 145 volts, the maximum field on the sample was no larger than 100 volts/cm.

D. Seebeck Voltage

Proper functioning of the equipment for measurement of the Seebeck voltage was verified by measuring the Seebeck voltage of intrinsic silicon up to 769°K and comparing the values to those published by Geball and Hull (19). The values were reproduced to within the experimental accuracy of their data.

The procedure was to use the voltage mode of operation of the electrometer (internal resistance = 10^{14} ohms) to measure the voltage between the copper blocks attached to the sample. Then, to eliminate the effects of induced voltages and to obtain higher accuracy, the measured voltages were plotted as a function of the temperature difference between the copper blocks, i.e., the ends of the sample.

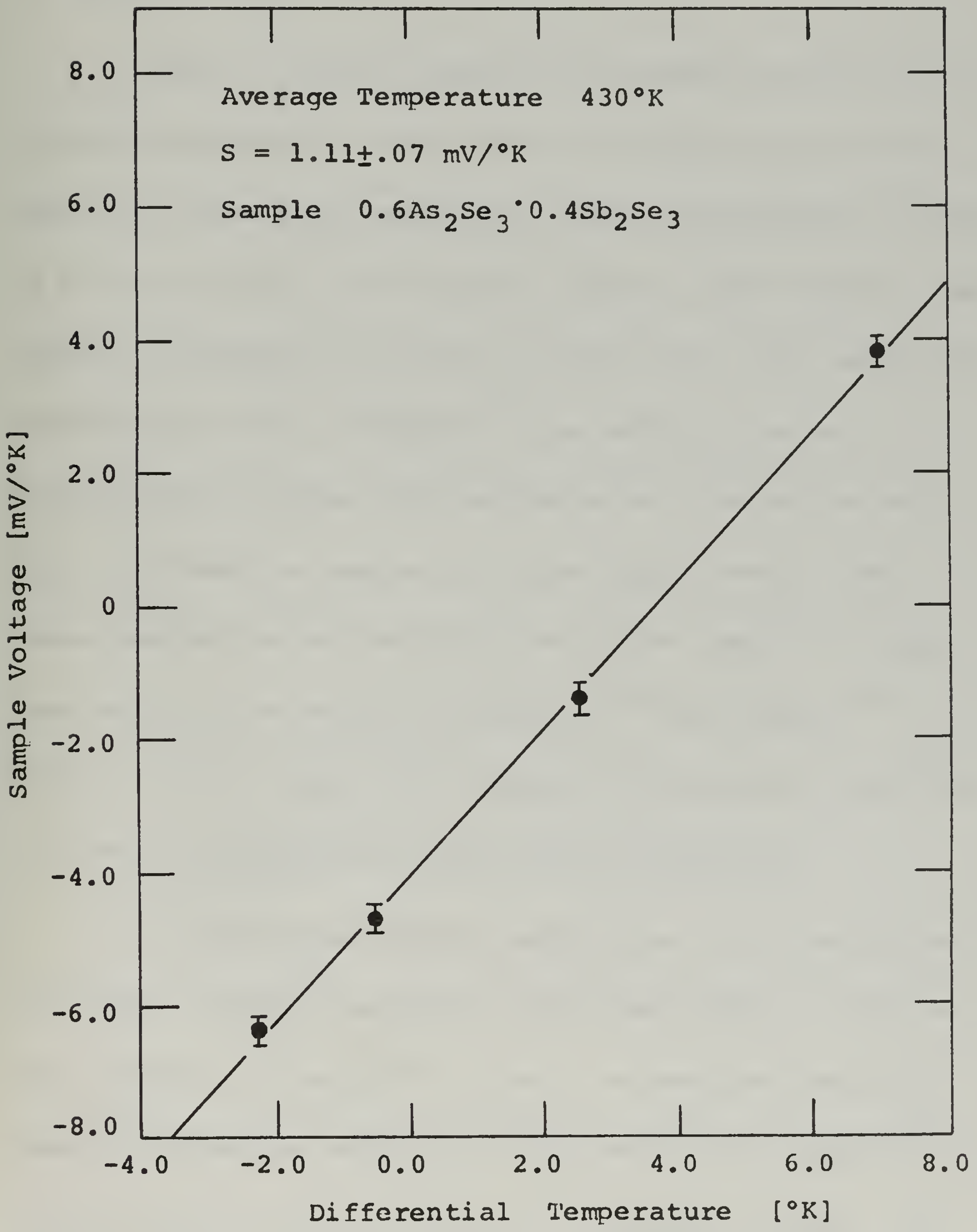
The measurements on silicon showed that the voltage measurements were accurate only if the temperature gradient was not time dependent, i.e., a steady state situation had been achieved. It was not necessary to correct the value of the voltage for the difference in Seebeck voltage of the leads because the correction was negligibly small. It was assumed that the contact Seebeck voltages between the ends of the sample and the copper blocks

cancelled each other.

Figure 3 shows a typical curve of measured voltage against T. Each point on the line represents values of temperature, temperature difference and voltage measured which were stable enough so that over a period of two hours the values did not change more than a few percent. The slope of the line is one data point of input into the Seebeck voltage versus reciprocal temperature plot, Figure 5 .

Figure 3

Sample Voltage vs Differential Temperature



Chapter IV

EXPERIMENTAL RESULTS AND DISCUSSION

A. Electrical Resistivity

Figure 4 displays graphically the measured resistivity at various temperatures for three samples. The samples were not all taken to the same upper temperature to avoid devitrification, however, as will be seen later, the $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ sample displayed some changes in properties as a result of being taken to high temperature (approximately 450°K). Platakis $^{(6)}$ has shown that the rate of devitrification increases with temperature up to the melting point, and occurs faster for samples with higher Sb_2Se_3 content. The values obtained for the resistivity activation energy, E_ρ, agree quite well with the results of Callaerts $^{(14)}$ and Platakis $^{(6)}$. Table 1 lists E_ρ values, the logarithm of the resistivity coefficent, ρ_o, and the thermoelectric power activation energy, E_s.

In the vitreous state the samples seem to be characterized by a single activation energy for a given composition. It will be shown, however, in Section IV. C, that if an amorphous sample is taken to temperatures where the devitrification rate is significant, the resistivity activation energy can be expected to change. The

Figure 4

Logarithm of the Resistivity vs Reciprocal Temperature

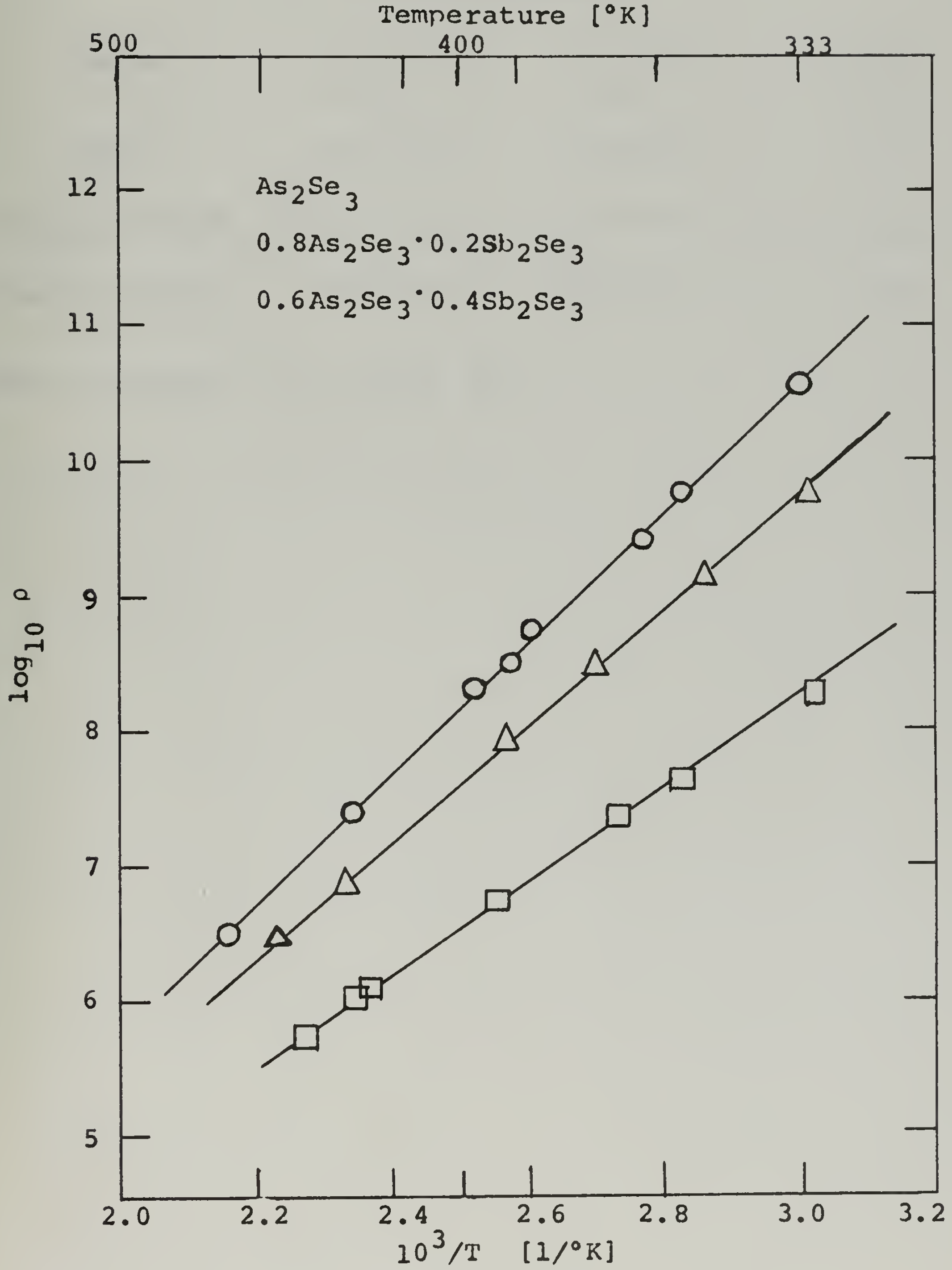


Table 1

ACTIVATION ENERGIES

Sample	E_ρ [eV]	E_s [eV]	log ρ_o
As_2Se_3	0.94 $\pm$0.03	1.03 $\pm$0.08	-3.70
$0.8As_2Se_3 \cdot 0.2Sb_2Se_3$	0.84 $\pm$0.03	0.78 $\pm$0.12	-3.02
$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$	0.76 $\pm$0.06	0.49 $\pm$0.10	-3.20

*Based on equation $\rho = \rho_o \exp(E_\rho /kT)$

modified sample is characterized by a single resistivity activation energy and yields a very linear log ρ vs 1/T plot over the temperature range covered in this work.

The temperatures are much too high and cover too narrow a temperature range to expect to see any $T^{-\frac{1}{4}}$dependence, and no attempt was made to fit the resistivity data to such a temperature dependence.

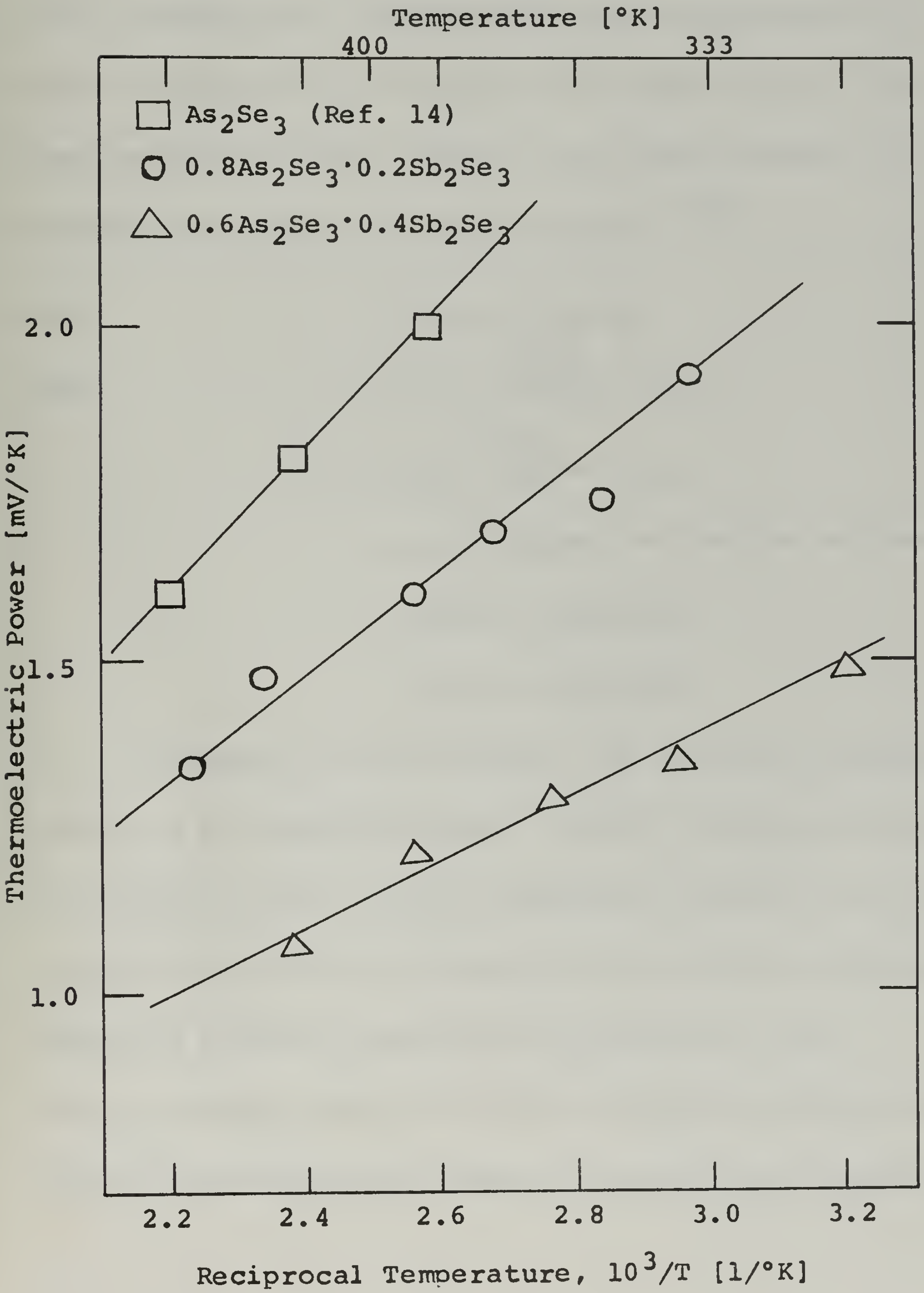
B. Seebeck Voltage

Figure 5 displays the results of the Seebeck voltage measurements. All values are positive, thus indicating that holes are the predominant carrier. The As_2Se_3 data is taken from Callaerts (14), since the data obtained during this work (presented in Appendix D) for the As_2Se_3 sample suffered from contact problems. (Although too low a value for S was obtained, the observed value for E_s, the thermoelectric power activation energy, was in good agreement with Callaerts' results.)

Only part of the data taken for the $0.6As_2Se_3 \cdot 0.4As_2Se_3$ samples is shown because of an apparent devitrification problem which was discovered during this work. This will be discussed in Section C of this chapter. It should be pointed out that the curve may thus be that of a structurally modified sample.

Figure 5

Thermoelectric Power vs Reciprocal Temperature



The three curves can be fit to a curve of the form (14),

IV.B.1
$$S = \frac{k}{e}\left(\frac{E_s}{kT} + a\right)$$

which corresponds to a theromoelectric power characteristic of conduction dominated by one highly mobile single carrier. The error bracketts for these curves are large enough, however, to accomadate many postulated curves of the form (14),

IVB.2
$$S = \frac{1}{\sigma}\left(\sigma_e S_e + \sigma_h S_h\right)$$

where
$$S_e = -\frac{k}{e}\left(\frac{E_C - E_F}{kT} + a_e\right)$$

$$S_h = \frac{k}{e}\left(\frac{E_F - E_V}{kT} + a_h\right)$$

a_e, a_h = constants for electrons and holes

$$\sigma = C_h \exp\left[-(E_F - E_V)/kT\right]$$

$$\sigma = C_e \exp\left[-(E_C - E_F)/kT\right]$$

Equation IV.B.2 above implies that two types of carriers are involved in the conduction process. However, the data fit an equation of the form of IV.B.1 to within experimental accuracy, and the thermoelectric activation energy obtained by this procedure confirms the resistivity activation energy, with the exception of the $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ sample. Even the last sample, however, is not very far from agreement and, based on facts which are presented in the

next section, its value of E_s may be higher than 0.49 eV. It can be concluded that E_s and E_ρ are equal in value for the fully amorphous $(1-x)As_2Se_3$·$x\,Sb_2Se_3$ system for $x = 0.0$ through $x = 0.2$, and it may tentatively be concluded that the equality continues through $x = 0.4$.

One implication of this conclusion is that conduction in this system is probably occuring by delocalized states since if the hopping mechanism for conduction (3) was present, the resistivity activation energy would be different from the thermoelectric power activation energy.

It is possible for these samples, based on Platakis' results, to assume that E_F lies in the middle of the gap. If Motts' results (21) are accepted, then

$$S = \frac{k}{e}\left[(E_F - E_V)_{T=0}/kT - \gamma/k + 1\right]$$

where γ is the thermoelectric power temperature coefficient.

For the samples measured in this thesis this results in

$$\gamma = 4.0 \times 10^{-4}\ \mathrm{eV}/^{\circ}\mathrm{K} \quad \text{for } 0.8As_2Se_3 \cdot 0.2Sb_2Se_3$$

and

$$\gamma = -0.2 \times 10^{-4}\ \mathrm{eV}/^{\circ}\mathrm{K} \quad \text{for } 0.6As_2Se_3 \cdot 0.4Sb_2Se_3.$$

Platakis(6) measured an average optical temperature coefficient of $\alpha = -6.6 \times 10^{-4}\ \mathrm{eV}/^{\circ}\mathrm{K}$ for both of the above combinations. (Recall that these can be compared only after γ is multiplied by -2.) The

x = 0.4 sample probably shows poor agreement because of the phenomenon discussed in the next section.

C. Anomalous Behavior of the $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Samples

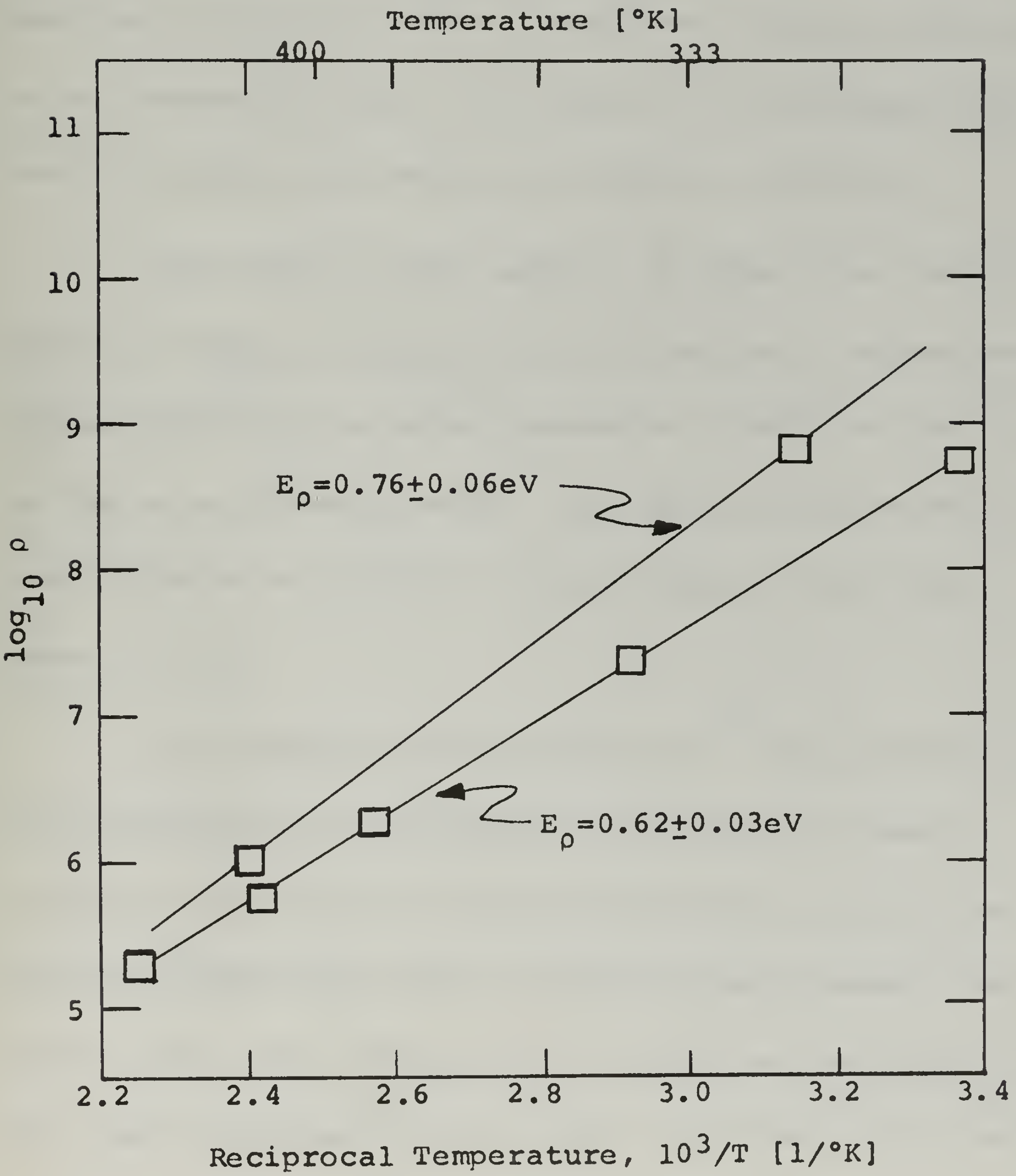
Figure 6 shows the logarithm of the resistivity vs reciprocal temperature for one of the $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ samples that was measured in this work. Points are labled 1 through 7 in accordance with their timed sequence of measurement. Points 1 and 2 were measured after the sample had been taken to an average temperature of 441°K (maximum temperature 445°K). Points 3 through 7 were measured after the sample had experienced an average temperature of 447°K (maximum temperature 450°K). A possible reason for the change in resistivity is that the sample has experienced a structural modification.

The slope and resistivity values represented by points 1 and 2 are in very close agreement with the results of Platakis (6) for samples which were known to be fully vitreous. It is presummed, on the basis of this agreement, that the sample is still predominantly vitreous even though it has experienced a maximum temperature of 445°K.

The thermoelectric power for this sample was measured as a function of temperature before the above resistivity, points 1 and 2,

Figure 6

Logarithm of the Resistivity vs Reciprocal Temperature for the Second $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Sample



were generated. These thermoelectric power values are plotted in Figure 7 as points 1 through 6, Sample 2, and can be presummed to represent predominantly amorphous $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$. Points 7, 8 and 9 of Figure 7 were made after the sample had experienced structural modification. Quite a significant change has taken place in the thermoelectric power. The change is far more dramatic than would be expected from looking at the change in resistivity.

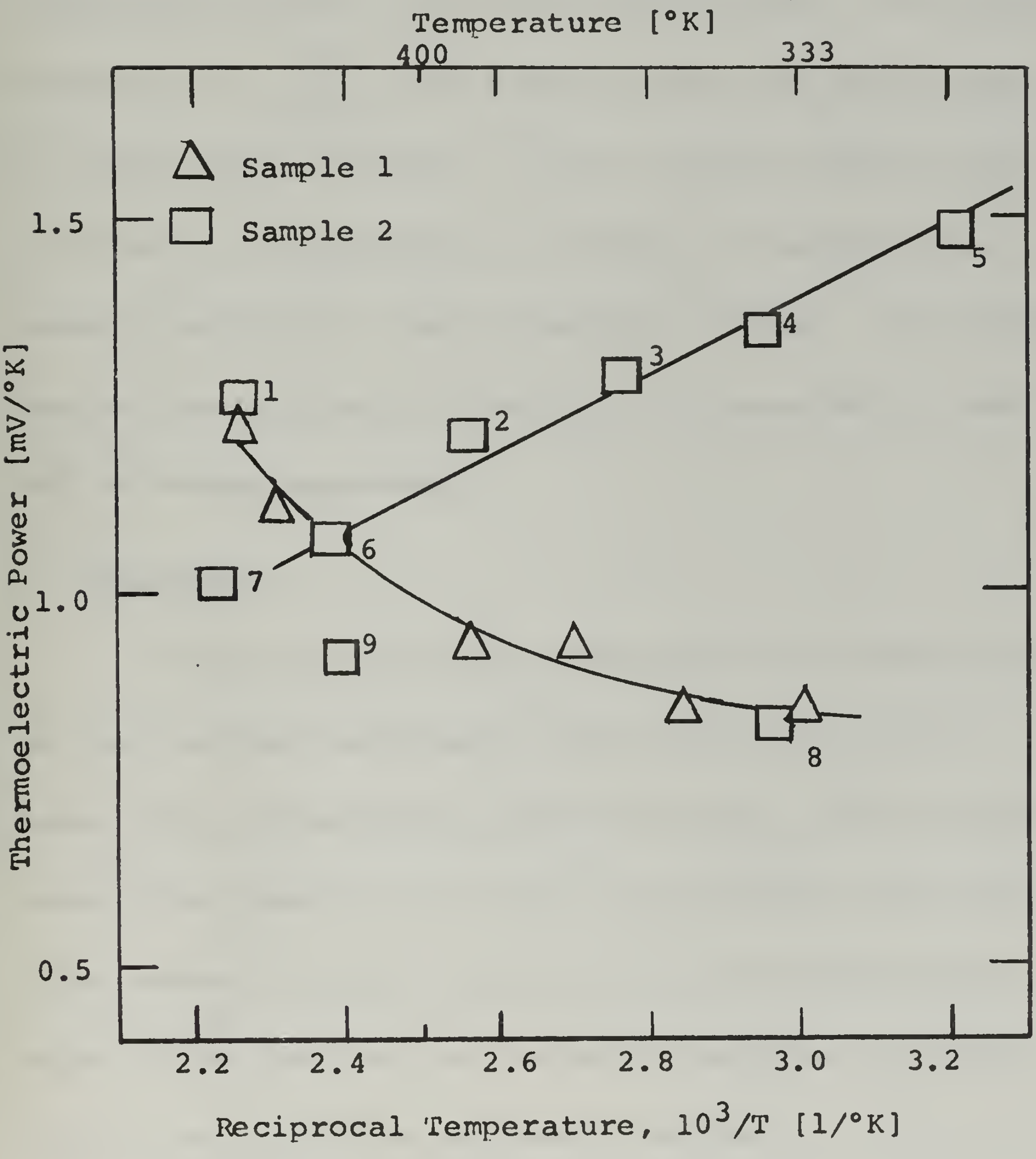
The remaining points, Sample 1, in Figure 7 are those of a sample of $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ which had experienced a maximum temperature of 447°K and an average temperature of 444°K for about twice as long as the preceeding sample. This modified sample shows value characteristics very similar to those of Sample 2 after it was heated to 450°K.

Devitrification studies by Platakis (6) show that the rate of devitrification at the temperatures experienced by these is sufficiently high that devitrification is probably a part of the structural modification which is causing the large changes in the thermoelectric power. Since, however, devitrification is associated with local crystallization of the sample, the effect of this partial devitrification on the thermoelectric power is quite baffling since neither crystalline As_2Se_3 or crystalline Sb_2Se_3 show increas-

Figure 7

Thermoelectric Power vs Reciprocal Temperature

for $0.6As_2Se_3 \cdot 0.4Sb_2Se_3$



ing thermoelectric power with temperature.

One possible cause for this temperature dependence of the thermoelectric power in this apparently partially devitrified sample is a temperature dependent Fermi energy which increases with increasing temperature, i.e., $\frac{\partial E_F}{\partial T} > 0$; however, there is no physical basis for postulating such behavior. Another possible explanation for this behavior is the formation of "islands" of degenerate semiconductor material in a "sea" of amorphous material. The resistivity would not be significantly affected but the thermoelectric power could be changed considerably.

D. Polarization

It was discovered during measurements of the Seebeck voltage that resistance measurements which used fields of about a hundred volts per centimeter polarized the sample. The polarization relaxed after removal of the field in an exponential manner with a time constant of about 110 minutes. The polarization was dependent on the amount of time the sample experienced the electric field but no quantitative measurements were made.

Chapter V

CONCLUSIONS

With regard to the work on the $(1-x)As_2Se_3$:x Sb_2Se_3 system accomplished by this thesis it is concluded that:

(1) Within experimental accuracy the activation energy for conduction and thermoelectric power are the same for concentrations x = 0.0 through 0.2. At x = 0.4, the measured values are not in exact agreement, but because of high probability that the samples measured have been partially devitrified even though they were not heated above the glass transition temperature, it is tentatively concluded that E_ρ and E_s are likely the same through at least x = 0.4.

(2) For the higher Sb_2Se_3 content materials the thermoelectric power is more sensitive than the resistivity to subtle structural changes which have occurred in the sample.

(3) The sample can be polarized with very low electric fields of about 100 volts per centimeter.

Chapter VI

SUGGESTIONS FOR FURTHER WORK

This investigation has raised some new questions concerning the relationship between E_ρ and E_s for amorphous semiconductors. In particular, the puzzling behavior of the $(1-x)As_2Se_3x\ Sb_2Se_3$ system in the vicinity of $x = 0.4$ needs further exploration and better documentation. Since vitreous samples can be made with $x = 0.45$, i.e., $0.55As_2Se_3 \cdot 0.45Sb_2Se_3$, it would probably prove useful and enlightening to study that combination in connection with the behavior of devitrified samples.

Some of the work accomplished by this thesis should be redone using new samples and using a modified procedure which measures the thermoelectric power starting at the lower temperatures.

The polarization noted in this work also represents a potential area for study. Polarization at such a low electric field has not previously been reported in the literature for the $(1-x)As_2Se_3 \cdot x\ Sb_2Se_3$ system.

The value of measuring more than one property of a material at a time on the same sample can not be underestimated. Very small changes in one property can easily go unnoticed or be attributed to

experimental error when, in fact, they are significant indicators of considerable changes taking place in the samples.

BIBLIOGRAPHY

1. R. Roy, J. Non-Crystalline Solids 3 (1970) 33-40.

2. D. Adler, Electronics, Sept 28, (1970) 61-72.

3. M. H. Cohen, J. Non-Crystalline Solids 4 (1970) 391-409.

4. T. J. Kobylarz, J. Non-Crystalline Solids 2 (1970) 515.

5. A. E. Owen, N. Clare and S. Frank, Abstracts of the conference on Low Mobility Solids, p. 109 (Sheffield, England, 1966).

6. N. Platakis, "Semiconducting Properties of the System (1-x)$As_2Se_3 \cdot x\ Sb_2Se_3$ in its Amorphous and Crystalline State, PhD Thesis, Dept. of Material Science, Mass. Inst. of Tech., 1970 (unpublished).

7. B. T. Kolimiets, Phys. Stat. Sol. 7 (1964) 359-372.

8. M. H. Cohen, J. Non-Crystalline Solids 4 (1970) 39-409.

9. A. I. Gubanov, Quantum Electron Theory of Amorphous Conductors, (Acadamy of Science Press, Moscow, 1963) (Translation by Consultants Bureau, New York, 1965).

10. L. G. Bailey, J. Phys. Chem. Solids 27 (1966) 1593-1598.

11. J. Stuke, J. Non-Crystalline Solids 4 (1970) 1-24.

12. T. N. Vengel, B. T. Kolomiets, Soviet Phys.-Tech. Phys. (1957) 2484.

13. Uphoff, H. L. and Healy, J. H., Semiconducting Properties of Inorganic Amorphous Materials, Journal of Applied Physics, Vol. 32, No. 5, May 1961, p. 950-954.

14. R. Callaerts, P. Nagels and M. Denayer, Phys. Letters 38A, 1, (1972) 15-16.

15. Johnson and Girdart, Bull. Am. Phys. Soc. 3 (1958) 232-233.

16. K. P. Braithwaite, Proc. Phys. Soc. (Lond) B64 (1951) 274.

17. J. Black, Phys. Chem. Solids 2 (1957) 240-242.

18. D. M. Chizhikov and V. P. Schastlivyi, Selenium and Selenides, Collet's (Publishers) Ltd, London, 1968.

19. F. H. Geball and G. W. Hull, Phys. Rev. 98 (1955) 940.

20. D. Adler, Critical Reviews In Solid State Science, 2 Issue 3 (1971) 317.

21. N. F. Mott, Phil. Mag. 24 (1971) 1.

22. R. P. Tye (editor), Thermal Conductivity, Academic Press, New York, 1969 (two volumes).

Appendix A

Table 2

SPECTROGRAPHIC ANALYSIS

(Furnished by American Smelting and Refining Company)

Impurities	Arsenic 99.999 +% Pure	Antimony 99.999 +% Pure	Selenium 99.999 +% Pure
Sb	N.D. *		
Tl	N.D.	N.D.	
Mg	< 1 ppm	< 1 ppm	
Mn	N.D.		N.D.
Pb	N.D.	1 ppm	N.D.
Sn	N.D.	N.D.	N.D.
Si	< 1 ppm	< 1 ppm	< 1 ppm
Cr	N.D.	N.D.	N.D.
Fe	N.D.	N.D.	N.D.
Ni	N.D.	N.D.	N.D.
Bi	N.D.	N.D.	N.D.
Al	N.D.	N.D.	N.D.
Ca	N.D.	N.D.	N.D.
Cu	0.1 ppm	< 1 ppm	< 1 ppm
In	N.D.	N.D.	
Cd	N.D.	N.D.	N.D.
Na	N.D.		
Zn	N.D.	N.D.	
Ag	N.D.	N.D.	N.D.
Te	N.D.		1 ppm
Hg	N.D.		N.D.
As			1 ppm
Halogen and S			< 0.0005% **

* N.D. denotes "nonedetected" by Standard Spectrographic Methods

** Chemical Analysis

Appendix B

EQUIPMENT AND MATERIAL PROBLEMS OF MEASUREMENT OF ρ, κ AND S

In anticipation of other workers continuing the study of this transport properties of the $(1\text{-}x)As_2Se_3{:}xSb_2Se_3$ system, several of the pitfalls of experimental techniques are presented. The following is broken into two major areas. The first is concerned with the apparatus and though some of the considerations are general in nature, most of them are specific to the equipment used. The second area of interest is the materials and how their properties cause difficulties in measurements.

The first major problem that was encountered after initial design and construction of the apparatus was that the tubing would occasionally break under vacuum. When this occurred at high temperature the No. 40 wires generally oxidized to dust. The problem was finally traced to the teflon end cap. Teflon had been used so that the feed-throughs would have very high resistance between circuits. The cap was 8mm thick in the direction of the axis of the tube and had an inner diameter of 51mm and an outer-diameter of 61mm (except for the O-ring groove) for the cylindrical

portion that fit 40mm over the glass tube. The glass tube would break because the vacuum would cause the end disc to deform slightly into a concave shape. This deformation caused an outward radial strain on the glass tube, placing it in tension. Even though the glass had been annealed the tension was great enough to cause breakage. The problem was solved by using a copper insert which sealed to both the glass tube and the teflon end cap but never put the glass into tension.

It is most common in experiments like these to measure temperature and differential temperatures with thermocouples. Sometimes the thermocouple is embedded into or attached to the sample. To keep parallel resistance paths to a minimum, the thermocouples for this apparatus were to be embedded in the copper blocks but electrically insulated from them. It was determined by measurements that Sauereisin ceramic cement with resistance of 10^5 to $10^6 \Omega$ to the block was not adequate. The final solution was the use of an alumina insert which was drilled to allow the thermocouple to be placed in a small cylindrical hole and cemented there with Sauereisen, and which was shaped to allow it to be inserted into another hole in the jaws of the copper blocks where it was also cemented by using Sauereisen. The use of the cement

improved the thermal contact but did not degrade the electrical resistivity.

Thermal conductivity measurements were abandoned because the copper blocks and bed plate assembly were of a very poor geometry for obtaining a linear guarded system which could accurately measure small values of $\kappa^{(22)}$. Guarding here refers to thermal guarding which reduces thermal leaks and blackbody radiation, a very serious source of error at other than cryogenic temperatures. It is not practical to attempt to measure high electrical resistivity, low voltage and low thermal conductivity using the same sample holder if wide ranges of temperature are involved.

Thermal steady-state and voltage steady-state problems, as mentioned in the main text, can introduce significant error into the measurements. It was necessary to use long periods of time to ensure that steady-state conditions existed before readings were accepted. A strip chart recorder was very valuable for this purpose because trends could be easily spotted on the chart.

The last equipment problem to be discussed is a problem that is common to all electrical measurements on highly resistive samples. The problem is induced voltages and grounding. A

common and good ground is an absolute necessity. Failure to have one will result in random drift in the voltage readings. The effects of induced voltages can be reduced by proper grounding, shielding and insulating. A couple of "tricks" can also be used. There are available some special sprays which reduce static electricity. The other trick is to keep all leads as short as practicable.

The sample itself can introduce experimental difficulties. The very brittle nature of the amorphous materials makes handling them a very sensitive operation. Experiments, in general, should be conducted in a manner which minimizes handling of the sample. Another problem which also stems from their brittle nature is that of making contact with the sample. The use of liquid silver (GC Electronics No. 21-2 Silver Print) in this experiment apparently adequately solved that problem, as silver adheres well to these glassy materials and also has good conduction properties, and does not seem to "block" conduction as, for example, aluminum does (20).

The use of an electrometer to directly measure the resistance of these samples is not advised because the Seebeck voltage is large enough and the sample current small enough when the internal electrometer power supplies are used that it affects the resistance

measurements.

Using a battery and an ammeter (electrometer) to measure voltage and current and thus calculate the resistivity is also not without problems. As noted in the results section, a field of about 100 volts/cm causes polarization which decays away with a half life of approximately 110 minutes. Millivolt measurements taken during this decay time will not be correct.

Appendix C

RESISTIVITY vs TEMPERATURE DATA

As_2Se_3		$0.8As_2Se_3 \cdot 0.2Sb_2Se_3$		$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Sample 1		$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Sample 2	
T [^{o}K]	$\log \rho$	T [^{o}K]	$\log \rho$	T [^{o}K]	$\log \rho$	T [^{o}K]	$\log \rho$
463	6.49	448	6.47	441	5.70	318	8.82
428	7.37	429	6.88	428	6.01	417	5.98
401	8.30	389	7.92	422	6.09	444	5.27
389	8.47	371	8.47	392	6.74	389	6.28
384	8.27	349	9.16	366	7.36	343	7.37
363	9.41	332	9.77	354	7.64	414	5.74
355	9.75	296	11.37	331	8.27	298	8.73
334	10.54						

Appendix D

THERMOELECTRIC POWER vs TEMPERATURE DATA

As_2Se_3		$0.8As_2Se_3 \cdot 0.2Sb_2Se_3$		$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Sample 1		$0.6As_2Se_3 \cdot 0.4Sb_2Se_3$ Sample 2	
T [°K]	S $[\frac{mV}{°K}]$	T [°K]	S $[\frac{mV}{°K}]$	T [°K]	S $[\frac{mV}{°K}]$	T [°K]	S $[\frac{mV}{°K}]$
473	.52	448	1.34	442	1.21	443	1.26
440	.68	427	1.47	431	1.11	396	1.21
397	.93	391	1.59	391	.93	363	1.29
368	1.14	373	1.69	370	.93	339	1.35
355	1.28	352	1.74	352	.84	312	1.48
		337	1.92	333	.85	420	1.07
						447	1.01
						338	.82
						418	.91

Thesis
C7596 Cox
134537
Transport properties
of several amorphous
semiconductors.